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Complexation of copper ions in atmospheric precipitation in Croatia

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Abstract

Organic complexation in atmospheric precipitation is an important control mechanism of the biogeochemistry of metal ions. We have measured complexation of copper ions in bulk precipitation by the method of differential pulse anodic stripping voltammetry (DPASV), which introduces least perturbation in the samples. The precipitation samples were collected periodically during one year in the mainland area of Croatia (Zagreb) and at the Adriatic coast (Šibenik). The results have shown the complexation of copper ions in all the samples. The method of determination presumes the existence of 1:1 copper ion - ligand complexes. The complexing capacity of rainwater samples for copper ions ranged between 0.010 and 1.4 μM . The highest capacity was measured in April 2003 in rainwater sample from the Šibenik area, which could be associated to the contribution of biogenically driven organics to marine aerosol. Apparent stability constants determined were in the range of 6.1 -10. The sources of organic ligands in the samples could be multiple. The concentrations of dissolved organic carbon (DOC) as well as of surface active substances (SAS) were measured. The proportion of complexing ligands in these two organic matter fractions has also been discussed.

Key words: bulk precipitation, electrochemical method, complexation, copper ion.

1. Introduction

Atmosphere is one of the major routes by which metal ions enter the aquatic systems (Jickells, 1995), which is especially true for the so called “atmophylic” metal ions (Stumm and Morgan, 1995) such as Pb^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Cu^+ and Ag^+ . The biogeochemistry of trace metals, especially in the atmosphere, is of utmost importance since they are as free metal ions involved in the catalysis of a number of atmospheric reactions such as the oxidation of SO_2 , the production of OH radicals and the cycling of iron (Sedlak and Hoigne, 1993). Inorganic

metal speciation in precipitation is a strong function of the source of aerosol and of aerosol's pH (Chester et al.1993, Zhang et al.2001, Zhang et al.2007). Although some studies have been performed in the nineties about the role of organic complexation in controlling trace metal speciation in rainwater and aerosols (Spokes et al., 1996, Cheng et al., 1994, Chester et al. 1993) as well as about its potential to modify metal solubility in precipitation (Zhuang and Duce, 1993) and further on in the aquatic environment, there is still little known about this important issue. Some authors studied trace metals presence and distribution in the precipitations (Berg et al, 1994; Gelinas and Schmit, 1998; Lawlor and Tipping, 2003). The organic matter composition was studied as well (Likens et al., 1983; Franz and Eisenreich, 1993; Chebbi and Charlie, 1996; Havers et al., 1998; Kiss et al., 2003; Orlović-Leko et al., 2004; O'Dowd et. al, 2004; Latif and Brimblecombe, 2004; Latif and Brimblecombe, 2005). However, the papers dealing with the interaction between the metal ions and organic matter are scarce (Spokes et al., 1996; Okochi and Brimblecombe, 2002). The source of organic complexants in precipitation is unclear and possibly there may exist multiple sources. Okochi and Brimblecombe, 2002, say that humic-like substances are the most likely ligands in the atmosphere and that a number of polycarboxylic acids and hydroxy forms (e.g. citric and tartronic acid) effectively complex the metals such as copper in atmospheric aerosols. Spokes et al., 1996, postulated the terrestrial origin of the ligands. In the paper Orlović-Leko et al., 2004, the presence of a substance similar to humic acid was found. O'Dowd et al., 2004, stressed the importance of biogenically-driven organic contribution to marine aerosols during the period of intensive biological activities. Some characterization of water-soluble organic compounds in rainwater and aerosols has been done (e.g. Likens et al., 1983; Decesari et al., 2000; Kiss et al., 2003; O'Dowd et al., 2004; Latif and Brimblecombe, 2004; Latif and Brimblecombe, 2005). Likens et al., 1983, analyzed wet precipitation for total organic carbon (TOC), dissolved organic carbon (DOC), particulate organic carbon (POC), carboxylic acids, aldehydes, carbohydrates, tannin/lignin, primary amines and phenols. DOC was partitioned into molecular weight ranges via ultrafiltration. Average summertime TOC concentrations were greater than average wintertime TOC concentrations. TOC concentrations were in the range 0.1 to 4.87mg/L, while DOC was in the range 0.07 to 3.10 mg/L. Regarding the molecular size distribution of DOC - the smallest size (<1000Da) was predominant, representing 37% to 49% of the TOC. Carboxylic acids accounted for the largest share of LWM (low molecular weight)-DOC (11% to 14% of TOC) (Likens et al.,1983). Characterization by proton nuclear magnetic resonance has shown that major proportion of DOC, i.e. 77%, is composed of polyols or polyethers, hydroxylated aliphatic acidic

compounds and highly unsaturated polyacidic compounds of predominantly aliphatic character with a minor content of hydroxyl groups (Decesari et al., 2000). The sources of these compounds in precipitation still remain to be clarified.

In this paper we determined the extent of the interaction of metal ions with the organic matter, (i.e. complexation), in bulk precipitation in the continental and coastal parts of Croatia. The interest is primarily focused on the complexation of copper, which forms very stable organic complexes, which is widespread in nature and represents an essential metal ion.

2. Materials and methods

2.1. Sampling and sampling locations

Samples were collected in the Šibenik area from January 2003 until February 2004 as bulk atmospheric deposition during the periods of different rain events. In the Zagreb area the samples were collected occasionally from February 2003 to February 2007. The collected precipitation volumes ranged from 300 ml to 1850 ml. The bulk atmospheric deposition (wet and dry) was collected directly into a brown glass bottle (volume 2500 ml) with a 240 mm diameter glass funnel. Glass parts were washed with chrome-sulphuric acid and several times washed with Milli-Q water (Millipore system, USA). Containers had been set up at the beginning of the precipitation event to avoid previous contamination. No special provision was made for collecting snow, which occurred only on 2 occasions. Immediately after the collection the samples were transported to the laboratory and all measurements were made within one or two days. The samples for DOC, after filtration through 0.7 μm Whatman GF/F filters, were preserved with the addition of HgCl_2 (10^{-5} M) and stored in dark and cold (4°C) until analysis.

Regarding the sampling locations (see the map of Croatia in Fig. 1) our first sampling location was the town of Šibenik (about 51000 inhabitants) situated at the Adriatic coast. Šibenik is an industrial centre with metalworking (iron alloys, aluminum production), although this has been reduced after the war activities in the nineties. In the area there exists also some shipping activity, including the transport of phosphate ores. Traffic (especially during the summer period) is significant. Tourism and mariculture have also been developed. The climate is Mediterranean, with warm summer and mild winter periods. South winds are quite often blowing in this area (Orlović –Leko et al, 2003). Our second sampling location was the city of Zagreb (at the location of the Ruđer Bošković Institute). Zagreb is the capital of Croatia, with approximately 1 million inhabitants, characterized by continental climate and precipitation distributed more or less uniformly all over the year (annual average amount of

precipitation is 896 mm, Orlović-Leko et al., 2004). Heavy traffic is the main source of organic pollutants, along with some chemical and pharmaceutical industry, domestic heating and thermal power plant.

2.2. Cu complexing capacity determination

The complexing capacity value for copper ions (CCu) was determined by using differential pulse anodic stripping voltammetry (DPASV). Electrochemical measurements were performed using an ECOCHEMIE voltammetric instrument connected to a Metrohm three-electrode cell (VA 663, Metrohm stand). The electrochemical system and the cell were computer controlled.

The working electrode was static mercury drop electrode (SMDE) with the surface area 0.54 mm^2 . Ag/AgCl (3M KCl) was used as a reference electrode and graphite stick was applied as a counter electrode. To record the voltammetric peak, DPASV was operated under the following experimental conditions: modulation time 0.04 s, interval time 0.31 s, modulation amplitude 25 mV and step potential 5mV. Copper ion solution was prepared from the $\text{Cu}(\text{NO}_3)_2$ salt (Merck, Germany).

The complexing capacity value was determined by the direct titration method with increasing amounts of copper ions added to 25 ml of rainwater at natural pH and to acidified solutions (pH= 1.8) (Plavšić et al. 1982). The equilibration time between each addition was 15 minutes (which was proved to be adequate for equilibration of copper ions, i.e. the peak height did not change after this period of time). If the results were presented as the metal ion free (M), on the x-axis, to the metal complexed ratio ($M/M_T - M$) on the y-axis (Ružić, 1982; Van den Berg, 1982) they should give a straight line the slope of which would determine the copper complexing capacity value (CCu) while the intercept on the y-axis would provide the information about the apparent stability constant (K_{app}). Inert complex for the applied method of DPASV is the one which does not dissociate during the time - scale of the measurement.

The natural pH of the samples varied to high extent. In the Zagreb area it was in the range from 4.34 to 7.02 (see Table 1). In the Šibenik area the pH varied in the range from 4.88 to 7.19 (see Table 1). In general higher pH values were measured in the samples from the Šibenik area.

2.3. Determination of dissolved organic carbon (DOC)

The DOC concentrations were determined by using a sensitive high temperature catalytic oxidation (HTCO) technique. A Model TOC-5000 System (Shimadzu) with high sensitive Pt catalyst and non-dispersive infrared (NDIR) detector for CO_2 measurements was used. The

DOC concentrations were determined in duplicates by filtering parallel samples (2 x 500 ml) through Whatman GF/F filters precombusted at 450° C for 5 h. The blanks for DOC were less than 3 % of the respective lowest detected concentration. For DOC measurement the samples were filtered (Whatman GF/F - pore size 0.7 μm), spiked with HgCl_2 solution for preservation and stored in a cold dark place until analysis.

2.4. Determination of surface - active substances (SAS)

SAS in rainwater samples were determined by electrochemical method, phase selective alternating current voltammetry (PSACV) (Ćosović and Vojvodić, 1987). The electrochemical instrument used was either a BAS (Bioanalytical systems, USA) or ECO-CHEMIE (The Netherlands) connected to a Metrohm glass, three electrode cell, applying a Kemula type hanging mercury drop electrode (HMDE)(surface area= 2.2 mm^2), Ag/AgCl (3M KCl) as a reference electrode and Pt wire as a counter electrode. To rainwater samples NaCl solution was added to make 0.55 M NaCl electrolyte solution. The method is based on the principle that adsorption of SAS causes a decrease of the double layer capacitance at the mercury electrode, which depends on the quantity and the hydrophobic properties of SAS (Ćosović and Vojvodić, 1998). The surfactant activity is expressed as equivalent to a model substance, i.e. in mg/L of Triton -X-100, which causes the same capacitance decrease as the SAS in the investigated sample. The reproducibility of electrochemical measurements for 100 $\mu\text{g/L}$ of Triton-X-100 was 5% (Ćosović and Vojvodić, 1987).

2.5. pH determination

pH was measured by standard electrode methods with a digital pH-meter, either a Model Delta-OHM HD 86-02 or a Metrohm digital pH- meter.

3. Results and discussion

Organic matter measurements in rainwater performed in this work includes the determination of copper complexing capacity (CCu). In Fig. 2 the complexing capacity determination of the rainwater sample from the Zagreb area (sample 18, Table1) is presented. In Fig.2A the recorded voltammograms of the increasing copper additions to the sample at natural pH are presented (the additions were from 0 to 220 nM of copper ion). In Fig 2.B the results of direct electrochemical titration are presented as the dependence between the added copper ions and the corresponding current for the acidified sample (pH=1.8- straight line) and

for the sample of natural pH (pH=5.33, ■). In Fig.2C the results from Fig.2B are presented after transformation (by dividing all the concentrations with the slope of the acidified solutions); they are presented as copper ion added on the x-axis vs. copper ion found on the y-axis. In the Fig.2.D the data from Fig.2.C are linearized by the method of calculation by Ružić-van den Berg (Ružić, 1982, van den Berg, 1982) which enables to calculate the copper complexing capacity value from the slope of the line (slope = $1/CCu$) and the apparent stability constant from the intercept on the y-axis (intercept = $1/CCu \cdot K_{app}$). For the sample presented, the CCu was $0.035 \mu M$ while $\log K_{app}$ was 9.2.

CCu of rain water samples varied between 0.066 and $1.4 \mu M Cu^{2+}$ for the Šibenik area samples and between 0.010 and $0.586 \mu M Cu^{2+}$ for the samples from the Zagreb area. As the pH values are in general higher for Šibenik area, so are the CCu values as well. This is the feature well-known from the titration of humic material, i.e. that at higher pH values more binding sites are available due to their higher dissociation (Plavšić and Čosović, 1994). The highest complexing capacity value was obtained for the sample from the Šibenik area in April 2003, amounting to $1.4 \mu M Cu^{2+}$. These could be connected to the start of the season of new biological activity since it is known that in the months of increased biological activities (the season spring / summer) in marine aerosols there is a significant contribution of organic matter originating from biological activity (up to 63 %) while in winter months this organic matter amounts to only 15% (O'Dowd et al., 2004). Complexing capacity values similar to the values obtained for rainwater were obtained for the Adriatic seawater samples (Plavšić et al., 1982, Plavšić, 2003) as well as for the selected samples from the Aegean Sea (Scoullou et al., 2004). The values for complexing capacity for these natural seawater samples were between 0.02 and $1.00 \mu M Cu$. The highest values for complexing capacity were obtained either as a consequence of phytoplankton activities in certain area or as a result of the presence of some other source of the organic ligands and/or inorganic particles and colloids which were not filtered off, and which could bind copper ions as well.

The relative stability of the formed Cu complexes could be compared through the apparent stability constants ($\log K_{app}$) values. The determined $\log K_{app}$ values for all samples are in the range of 6.1 - 10. The highest $\log K_{app}$ value for the area of Šibenik is 8.1. Two $\log K_{app}$ values of 9.2 and 10 were calculated for the precipitation samples from the Zagreb area. High $\log K_{app}$ values indicate the presence of organic ligands which more specifically bind copper ions. The stability constants determined for model humic and fulvic substances are in the range of 6.5 - 8.4 (Plavšić et al., 2006).

Additional information on the organic ligand characteristics in seawater may be obtained by examining the complexing capacity values data normalized in terms of the DOC concentrations (CCu/DOC) measured in the same samples (Mantoura, 1981; Scoullos et al., 2004) (Table 1). Higher values of normalized concentrations of the complexing capacity for copper in relation to the dissolved organic carbon were calculated in the samples from the Zagreb area in winter (Feb. 2003 and Feb. 2005; 0.47 and 0.49, respectively), when the precipitation was in the form of snow. In these samples, which were not filtered, there were probably also present the particles, which additionally bound copper ions. For the Šibenik area the highest calculated CCu/DOC value was obtained in April 2003 (0.91, Table.1), which coincided with the value of the highest complexing capacity. It follows that the dissolved organic ligands in rain samples have more copper complexing sites available in spring time, when marine aerosols contain more ligands originating from biological activities. The lowest CCu/DOC values for the Šibenik area were detected in January 2003 and February 2004, i.e. in winter months. In the paper Kiss et al., 2003, the average molecular weight of humic-like substances (HULIS) in the atmospheric aerosols are determined to be in the 200-300 Da range. If taking into account our mean DOC value of all samples $\sim 2\text{mg/L}$, the supposed mean molecular weight of 250, and our CCu values which are in the range of 0.01 - $1\mu\text{M}$, we could calculate the percentage in mass of organic carbon (DOC) which is complexed by copper ion. These percentages in mass of DOC are in the range from 0.12 % to 12.5 %. Of course, this is only a speculative calculation and conclusion. The percentages can greatly change if the supposed mean molecular weight of ligand is different.

The value CCu/SAS , i.e. the complexing capacity values data normalized to surfactant activity of the same rainwater sample, provides the information on the complexing capacity of the part of the organic matter exhibiting at the same time surface- active properties (Table 1). For the Šibenik area the highest value was calculated for the sample from April 2003 (10.00) and for the Zagreb area it was calculated for snow sample from February 2005 (6.51). In Figs.3 (A and B), where the relationship between the complexing capacities and DOC (Fig. 3A) as well as the relationship between the copper complexing capacities and SAS (Fig. 3B) are presented, it can be seen that higher complexing capacity value does not at the same time necessarily mean higher SAS and/or DOC values and vice versa. This means that the ligands responsible for complexing copper are not proportional to DOC and/or ligands with surface active properties. In Fig.4 the ranges of complexing capacity values for different compartments in the coastal marine environment are presented, i.e. in the rainwater, in sea - surface microlayer samples (which comprises sea - surface layer up to 150-200 μm thick),

seawater samples and in the samples with exudates from algae released and/or present due to their decomposition (outliers are shown as black dots). Data for algae, sea- surface microlayer and seawater are taken from the papers Scoullos et.al., 2004 and Plavšić et al., 2007. It can be seen that the highest values for complexing capacity data are obtained for algal samples, so it is a plausible explanation that with present higher biological production in the sea due to the presence of algae and/or their decomposition products, there is also present higher amount of organic ligands in the precipitation originating from these coastal areas. There is a contribution of biogenically-driven organic matter in marine aerosol due to increased biological activities in the adjacent seawater.

4. Conclusion

The results obtained point to the existence of a dissolved organic carbon pool in precipitations with ligands capable to complex copper ions. Only a part of ligands exhibit surface - active properties and not necessarily all of them complex copper ions. Copper ions are complexed in all samples and the complexation determined is rather significant. Apparent stability constants amount up to $\log K_{app} = 10$, which indicates the presence of some ligands more specific for binding the copper ions. The percentage in mass of DOC complexed with copper in the precipitation samples is up to 12%. The difference exists in the precipitations from the continental part of Croatia (Zagreb area) and from the coastal zone (Šibenik area). In the area of Šibenik were determined higher complexing capacity values, which is the consequence of biogenically driven organic contribution to the precipitations.

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Figure captions

Fig.1 Map of Croatia with two sampling locations denoted: Šibenik (a port town, with developed tourism, shipping activity and metalworking industry) at the Adriatic coast and Zagreb (the capital of Croatia with heavy traffic, chemical and pharmaceutical industry and thermal power plant) in the mainland .

Fig.2 (A) voltammograms of increased copper ion additions to the sample no. 18 (Table 1.) pH =5.33, $E_d = -0.6$ V, $t_d = 60$ s; (B) Direct titration curves of rain sample (line: pH=1.8, ■: pH=5.33) copper concentration added vs. current measured; (C) Titration curves from (B) presented as copper ion conc. added vs. copper ion concentration found; (D) Linearization of the titration curves from (C) according to Ružić-van den Berg method from which CCu and log K were calculated.

Fig.3 (A) CCu (μ M) presented vs. DOC (mg/L) ; (B) CCu (μ M) presented vs. SAS(mg/L eq. Triton-X-100) (○- samples from Zagreb,●- samples from Šibenik).

Fig.4 Ranges of CCu (μ M) for different environmental compartments: rainwater, seawater, sea surface microlayer and algal exudates (the median is plotted and 90th percentiles with error bar).

No.	Date of sampling	pH	DOC mg/L	SAS eq. mg/L T-X-100	CCu μ M	log K	CCu/DOC μ M/mg/L	CCu/SAS μ M/mg L ⁻¹ eq. T-X-100
1	30.01.2003	7.16	1.48	0.090	0.066	7.1	0.04	0.73
2	22.04.2003	7.19	1.54	0.140	1.400	6.7	0.91	10.00
3	30.06.2003	6.56	3.18	0.320	0.360	7.0	0.11	1.13
4	28.08.2003	5.99	3.23	0.220	0.370	8.1	0.11	1.68
5	17.11.2003	5.90	2.49	-	0.440	7.6	0.18	-
6	27.11.2003 *	6.29	1.02	0.150	0.200	7.6	0.19	1.33
7	27.11.2003	6.72	0.89	0.160	0.110	-	0.12	0.69
8	11.02.2004	4.88	1.84	0.600	0.137	-	0.07	0.23
9	4/5.02.2003 Δ	7.02	1.08	0.080	0.510	6.1	0.47	6.37
10	10/11.04.2003	5.23	3.96	0.110	0.031	8.3	0.01	0.28
11	20/21.05.2003	4.73	2.68	0.110	0.110	-	0.04	1.00
12	31.08.2003	5.68	3.13	0.240	0.010	-	0.003	0.04
13	02.02.2005	4.66	5.53	1.165	0.396	7.1	0.07	0.34
14	21/22.02.2005 Δ	4.44	1.19	0.090	0.586	8.8	0.49	6.51
15	5/6.07.2005	4.70	1.39	0.075	0.137	-	0.09	1.83
16	29/30.09.2005	4.77	0.72	0.090	0.026	-	0.04	0.29
17	29/30.11.2005	4.65	0.98	0.125	0.011	6.7	0.01	0.09
18	22/23.01.2007	4.34	2.12	0.135	0.035	9.3	0.02	0.26
19	7/8.02.2007	5.02	2.33	0.150	0.069	10.0	0.03	0.46

TABLE 1.

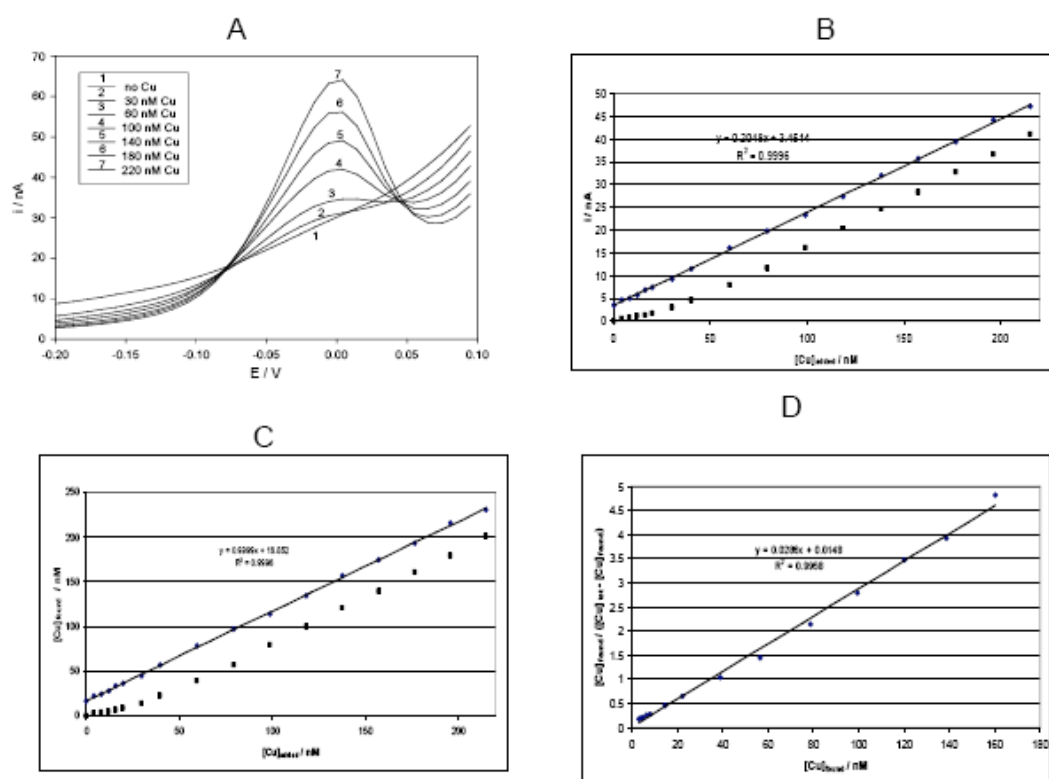
Precipitation data for coastal and mainland areas of Croatia. Data on the dates of sampling, types of precipitation, pH, dissolved organic carbon (DOC), surface active substances (SAS), complexing capacity (CCu), the corresponding log K, CCu/DOC and CCu/SAS.

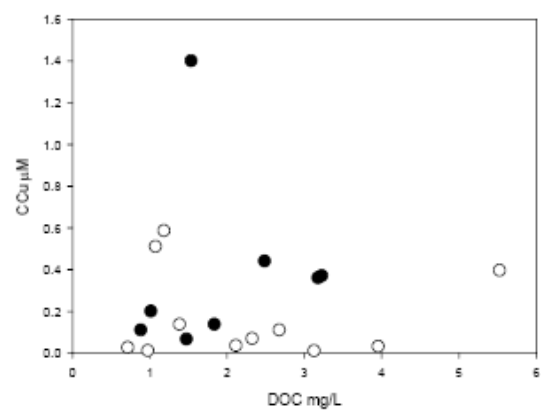
1-8 Samples from the Šibenik area – marine station (*; Šibenik – centre of town)

9-19 Samples from the Zagreb area (Δ snow); (-) not possible to calculate

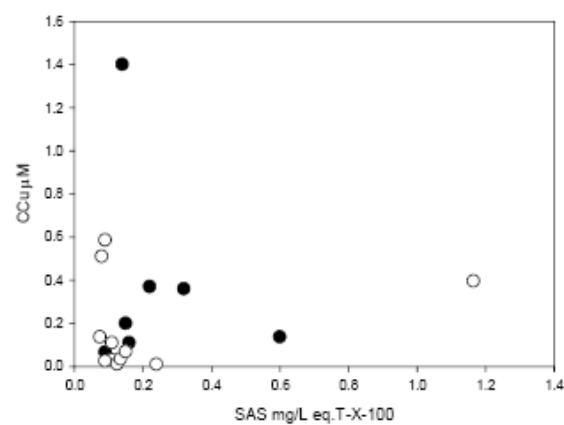
Figure







A



B

